



Novel acidic eutectic mixture as peroxidase mimetics for oxidative desulfurization of model diesel

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ABSTRACT

A new generation of green solvent, deep eutectic solvents (DESs), are being received increased interest in the fields of organic synthesis, electrochemistry, catalysis and oxidative desulfurization (ODS) process. Despite possessing high ODS activity, little is known for the mechanism of the excellent desulfurization performance of DES. In this study, a class of acidic eutectic mixture was prepared with different molar ratios of acetamide and glutaric acid. It was found that desulfurization process was significantly affected by the composition of prepared DES. Under optimal conditions, the desulfurization efficiencies of acetamide/glutaric acid (molar ratio 1 : 2) DES was capable to reach up to 99% within only 3 h. Density functional theory (DFT) calculation revealed that acetamide/glutaric acid DES possessed intrinsic peroxidase-like property and reduced greatly TS barriers in oxidation process. The synergy cooperation of acetamide and carboxylate like the active site of enzyme, achieving the catalytic oxidation of dibenzothiophene (DBT). In addition, this DES system was successfully applied for the deep oxidation desulfurization of real fuels, which demonstrated extraordinary catalytic performances.

1. Introduction

It is well-established that the emission of SO_x , NO_x , and particulate matter in exhaust gas not only cause acid rain and damage the ozone layer but also corrode metal equipment. Among them, sulfur oxides (SO_x) from combustion fossil fuels (coal, petroleum and natural gas) are regarded as one of the most significant sources of air pollution [1,2]. In recent years, with the increasingly restrictive strength in energy-saving and emission-reducing policy, the worldwide countries have successively proposed stringent requirements for the sulfur content in fuel. Therefore, deep desulfurization is becoming an urgent research topic [3–6]. For instance, the US Environmental Protection Agency (EPA) reduced the limit for sulfur content of diesel fuel low to 15 ppm in 2006 and the EU legislation set the upper limit of that to 10 ppm in 2009 [7,8]. China enacted the Chinese National V Standard, attempting to reduce the sulfur content in oils below to 10 ppm on April 1 st, 2016 [9].

At present, hydrodesulfurization (HDS) is a traditional and mature desulfurization technology [10]. However, it must be carried out under

high temperatures and pressures, which makes it costly for deep desulfurization in refineries. In addition, the HDS is difficult in removing organic sulfides with larger steric hindrance, such as 4,6-dimethylbenzothiophenes (4,6-DMDBTs) and its derivatives [11–13]. As a complementary approach, oxidative desulfurization has been paid more and more attention nowadays. It not only possesses prominent removal efficiency for sulfur compounds, in particular for some aromatic sulfur compounds, but also can be carried out under mild conditions [14–18]. These heterocyclic sulfides can be oxidized to polar sulfones that are easily removed by extraction or adsorption. Ionic liquids as an extractants and catalysts with many advantages such as low vapor pressure, low volatility and good thermal stability have been successfully applied in different desulfurization processes [7,11,16]. However, the disadvantages of high cost and low biodegradability limit its widespread use on an industrial scale [19–21].

Deep eutectic solvents (DESs) are a new type of green extraction solvents, which are formed by two or three low-cost and safe components through hydrogen bond interaction [22]. With low price, easy preparation from natural available starting materials and the

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biodegradable, DESs not only show the physicochemical properties similar to those of traditional ionic liquids, but also overcome some of their disadvantages. They can be employed in a wide range of fields such as extraction [23], separation [24], catalysis [25], and electrochemistry [26]. Recently, many researchers reported that various types of DESs have been used in some promising desulfurization process [27–36]. For example, Li Changping' group utilized the tetramethyl ammonium chloride/polyethylene glycol (TBAC/PEG) as an extractant for the removal of benzothiophene (BT), giving rise to the extraction efficiencies of TBAC/PEG as high as 82.8% for one cycle [27]. Besides, they also designed a series of three-component 'metal ions' based deep eutectic solvents (MDESs) as extractants and TBAC : PEG : FeCl₃ based MDESs achieved the highest activity with 89.53% desulfurization efficiency [28]. Then Li Huaming' group used a choline chloride-based DES as a catalyst for desulfurization of fuels, affording the DBT removal efficiency up to 99.1% with the addition of H₂O₂ [29]. Very recently, our group innovatively synthesized a series of oxalate (OXA)-based DESs as catalysts for oxidative desulfurization of DBT using hydrogen peroxide as an oxidant. Noted that an DES with a OXA/TBAC molar ratio of 2 exhibited outstanding performance under mild conditions [30]. In addition, we reported on a combined (L-proline based DES coupled with H₂O₂) extraction coupled catalytic oxidative desulfurization (ECODS) system showing nearly complete (99%) removal of DBT at 60 °C in 2 h [31]. Our group also prepared a series of caprolactam-based acidic DESs for ODS. The experiment results demonstrated that the catalytic activities of ODS system were tightly associated with the DES composition [32]. In those works, it has been confirmed that the carboxylic acids in DESs are firstly oxidized to peracids by hydrogen peroxide, and then the peracid is used to oxidize S-compounds to the corresponding sulfones. However, direct oxidation of the carboxylic acids by the stoichiometric hydrogen peroxide is difficult due to the higher energy barriers [37–39].

Typically, peroxidase, as an important enzyme and an efficient biocatalyst, is capable of catalyzing the oxidation of aromatic compounds with H₂O₂ as the oxidant, which contribute to change of color or reduce toxicity of aromatic compounds [40]. However, as a kind of nature protein, peroxidase is not stable because of its denaturation under harsh environmental conditions. Especially, the enzymatic structure may be partially or completely destroyed and then lose catalytic activity under some harmful conditions [40,41]. Hence, the development of peroxidase mimic with excellent catalytic performance and environmental stability as substitutes of peroxidase is an urgent need but still a significant challenge [42].

In this manuscript, a series of DESs were readily synthesized, which served as extractant and catalyst for deep desulfurization of diesel using environmentally benign hydrogen peroxide as oxidant. It was found that both the composition of the DES and the molar ratio of acetamide to glutaric acid had influences on the catalytic performances during the desulfurization process. With purpose of giving an deep insight into the oxidation mechanism, the DFT calculation was performed, unravelling that the transformation of acetamide to ethyleneimine-2-nol was capable to apparently decrease the reaction barrier of H₂O₂ oxidation of glutaric acid. Herein, the –COOH group in acetamide/glutaric acid system was more easily oxidized into peroxycarboxyl groups in comparison with the direct peroxidation of carboxylic acid with H₂O₂ due to the lower reaction energy (127 kJ/mol) than the latter (273 kJ/mol). These results indicate that acetamide/glutaric acid DES as efficient enzyme-like catalyst play an important role in making the –COOH group capable of being easily oxidized into peroxycarboxyl groups by H₂O₂, confirming that this DES system is a robust and efficient enzyme-like catalyst system.

2. Experimental Methods

2.1. Materials

Acetamide and 4,6-dimethylbenzothiophene were purchased from Sinopharm Chemical Reagent (Shanghai, China). Oxalic acid dehydrate, glutaric acid, dibenzothiophene and benzothiophene were obtained from Macklin Reagent (Shanghai, China). Malonic acid was purchased from Civi-Chem Technology Co., Ltd. (Shanghai, China). Succinic acid was purchased from Tianjin Bodi Chemical Co., Ltd. Adipic acid was purchased from Wuxi Merkel Fine Chemicals Co., Ltd. All chemicals in our experiments were analytical reagent grade and used as received without further purification.

2.2. Preparation and characterization of deep eutectic solvents (DESs)

Acetamide (AC) was utilized as the hydrogen bond accepter (HBA) and four kinds of organic acid (oxalic acid dehydrate (OA), malonic acid (MA), succinic acid (SA), glutaric acid (GA) and adipic acid (AA)) were selected as the hydrogen bond donor (HBD). The two ingredients were stirred vigorously at a molar ratio of 1 : 2 at 80 °C in a round-bottomed flask. In particular, for AC and GA system, the eutectic mixtures were obtained by mixing AC with GA at molar ratios of 1 : 1, 1 : 2, 1 : 3, and 2 : 1, respectively. The mixture was stirred vigorously in an oil bath at 80 °C for one hour to obtain homogenous transparent liquid. The resultant products are designed as AC/GA, AC/2GA, AC/3GA, and 2AC/GA, respectively.

The infrared spectroscopy of sample was performed on Shimadzu IRAffinity-1S FT-IR spectrometers using KBr pellets. ¹H NMR spectra were measured on a Bruker DRX type spectrometer at room temperature (400 MHz) and internally referenced to tetramethylsilane signal in (CD₃)₂SO.

2.3. Oxidation desulfurization of model diesel

Model diesel (S content, 500 ppm) was prepared by dissolving one corresponding model sulfur compound, including BT, DBT and 4,6-DMDBT in n-octane, tetradecane was used as the internal standard. In a typical run, 2 mL of acetamide/glutaric acid DES, 10 mL of model diesel, and 0.106 mL of hydrogen peroxide (30 wt %) were added in a 50 mL round bottom flask. Subsequently, the mixture was stirred vigorously at 60 °C for 3 h. The upper oil phase was sampled periodically and analyzed for sulfur content by GC-FID (FuLi 9750, HP-5). The S-compound product was identified by GC-MS (Agilent 7890/5977B-GC/MSD; PONA).

2.4. Oxidation desulfurization of real diesel

The ODS performance of the CH₃CONH₂/HOOC(CH₂)₃COOH was also evaluated using a real diesel with initial S-content of 24 ppm. The sulfur compounds in the original diesel are mainly composed of DBT and their derivatives. The desulfurization process was similar to that of model oil. Typically, 10 mL DES, 10 mL commercial diesel, and 0.4 mL hydrogen peroxide were added into a 50 mL round bottom flask. The mixture was stirred vigorously at 60 °C for 3 h. The concentration of S-compounds of original and treated diesel was determined by microcoulometry (detection limit, 0.1 ppm). Detailed chemical analysis was analyzed by GC-FPD (Agilent 7890B; HP-5, 50 m × 0.25 mm i.d. × 0.25 μm; FPD: Agilent).

2.5. Computation and methods

Using WB97XD functional at 6-311+G (d, p) basis set level, the interaction of acetamide with dicarboxylic acid to form eutectic solvents (DES) was investigated. And we further optimize the reactants, intermediates, transition states (TS) and products in the oxidation

reaction of DBT with H_2O_2 as oxidants in the DES of acetamide and glutaric acid. Frequency calculations were done at the same level to confirm the correct character of transition states. All geometry optimizations and TS calculations were carried out using the Gaussian 09 program.

3. Results and discussion

3.1. Screening of DESs

Due to the good comprise between computational simplicity and accuracy, density functional theory (DFT) has been frequently used for electronic structure calculations where the generalized gradient approximation (GGA) method is usually employed to describe the exchange-correlation items. However, the conventionally GGA, e.g., PBE [43] or hybrid GGA functionals, e.g., B3LYP [44] are failed to capture dispersion interactions. In the DES system, the dispersion forces and hydrogen bonds play important roles, neglecting them may lead to incredible results, thus in this study, we employed the improved hybrid GGA WB97XD functional which has included long-range dispersion correction [45].

The Van der Waals interactions and hydrogen bonds are proposed to contribute a lot for the DES solvent effect [46,47]. Using the DFT method, we investigate the interaction of acetamide with dicarboxylic acid. As seen from the experiments, with a 1 : 2 ratio of acetamide to dicarboxylic acid, only the system of acetamide and glutaric acid shows the DES properties at 80 °C. By optimizing one molecule of acetamide interacting with two molecules of dicarboxylic acid (Fig. 1), it was observed that the hydrogen bonds are easy to form. As for smaller

molecules, such as oxalic acid and malonic acid, three H bonds are formed between the acetamide and dicarboxylic acid. But for dicarboxylic acids with longer chains, acetamide interacts through only two H bonds, the two carboxylic acids can obtain additional stabilized energy by the interaction between two alkyl chains, as well as the H bond between carboxylic acids.

It can be seen from Fig. 1a and 1b that the length of H bond between O and carboxyl is much shorter than that between O and amine owing to the less positive charges on the H atoms connected with N atom. However, the H bonds between two carboxyls are elongated to 2.027 and 1.881 Å in Fig. 1c and e, respectively, which can be attributed to the tension effect of molecules. The molecular tension also results in the elongation of H bond distance between carbonyl of acetamide with carboxyl and the shortage of H bond between amine with O in Fig. 1e.

Table 1 presents the melting point of different molecules and the interaction energy of acetamide with dicarboxylic acid. It is proposed that the H bonds between two solvent molecules are favorable for the formation of DES solvent. From the DFT calculation results, it notes that the H bond between acetamide and dicarboxylic acid are easy to form for all five dicarboxylic acids. And they all show strong interaction with the stabilized energy over 1 eV. Surprisingly, only glutaric acid shows the DES effect. It is inferred that the matching of melting points may be the key point. It can be seen that glutaric acid possesses a relatively low melting point of 95–98 °C, which is close to that of acetamide (85 °C), in comparison to all other dicarboxylic acids. Owing to the weak interaction between glutaric acid molecules, the acetamide is easy to enter the network of glutaric acids to form the mixture and decrease the melting point, so as to form the DES solvent.

A series of different oxidative desulfurization systems using AC/GA DESs as extractants and catalysts, H_2O_2 as oxidant are demonstrated in

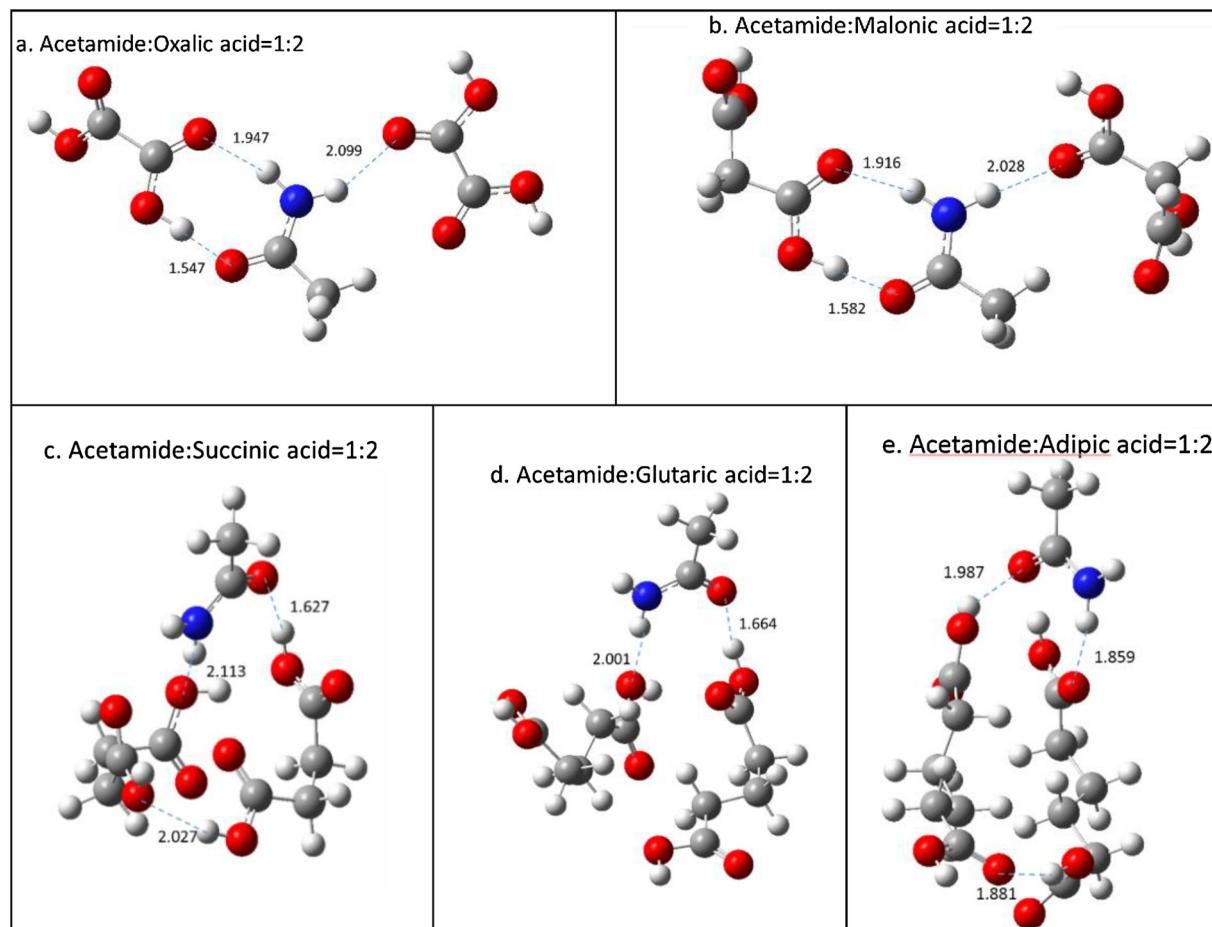


Fig. 1. The optimized structures of acetamide interacted with dicarboxylic acid in the ratio of 1 : 2. The unit of H bond length is Å.

Table 1
Screening of HBA and HBD^a

HBA		HBD		Interaction energy/eV	Appearance at 80 °C
Name	Melting point/°C	Name	Melting point/°C		
AC	82.3	OA	101~102	-1.117	Turbid white liquid
AC	82.3	MA	135~136	-1.076	White solid mixtures
AC	82.3	SA	185	-1.275	White solid mixtures
AC	82.3	GA	95~98	-1.058	Colorless liquid
AC	82.3	AA	152	-1.371	White solid mixtures

^a Reaction conditions: HBA : HBD (molar ratio) = 1: 2, T = 80 °C, t = 1 h.

Table 2. It can be found that the removals of DBT nearly can't be proceeded in the absence of hydrogen peroxide. After adding hydrogen peroxide, DBT was also hard to remove when only AC or GA was utilized as the catalyst (entry 5 and 6). It is important to highlight that once AC/GA DES was introduced into the reaction systems, the catalytic activity was enhanced dramatically in the presence of H₂O₂. Additionally, the desulfurization performance was closely related to the molar ratios of AC/GA DES. Unpredictably, with the GA molar content in the DES system increasing, a “volcanic type” profile of the sulfur removal was observed. When the molar ratio of GA/AC was 2, the removal efficiency of DBT reached maximum (99%) within 3 h (entry 3). **Fig. 2** presents the optimized structures under different ratios of acetamide to glutaric acid, and the DBT molecule interacting with these DESs. The interaction energy is listed in **Table 2**. Owing to the formation of H bond, the DES molecules have stronger interactions each other. With the increase of solvent molecules from 2 to 4, interacting energies increase from -0.744 to -1.850 eV. Meanwhile, their interactions with DBT only increase from -0.592 to -0.878 eV mainly through Van der Waals forces. Thus the DES system has only weak extracting ability to DBT.

3.2. Characterization of the AC/GA DES

Infrared spectra of AC, GA and AC/GA were collected, as shown in **Fig. 3(A)**. Compared with AC, the redshift of DESs peaks of carbonyl group (from 1680 cm⁻¹ to 1659 cm⁻¹) were clearly observed, likely due to the formation of hydrogen bonds [27]. Comparing GA with AC/GA, the C=O characteristic peak of carboxylic acid was blueshifted from 1698 to 1709 cm⁻¹. It is generally accepted that organic acids usually present in the form of dimers while the strength of the H bond between the acid molecules becomes stronger with the increase of carbon chain length. Longer carbon chain induces stronger ultra-conjugation effect, which causes more negative charge to be distributed on O atoms. Therefore, stronger hydrogen bonds are formed. The H-bonds strength between AC and GA may be weakened because of strong hydrogen bonds between acid molecules, resulting in the blue shift of the C=O group peak in IR spectra [34].

To further confirm the interaction between AC and GA, the ¹H NMR spectra of AC, GA and AC/GA are shown in **Fig. 3(B)**, the sharp and intensive H signal at about 12.07 ppm, attributed to H species in carboxyl groups, shifted to 12.09 ppm of weak and broad band after the formation of DES. This result suggested that the micro-environment of hydrogen atoms in carboxyl groups became complex, perhaps resulting from the formation of the hydrogen bond [27,38]. Since the hydrogen-bonded oxygen atoms are electrophilic, the electron density of the hydrogen atoms is decreased, further causing the downshift of the chemical shift.

3.3. Desulfurization performance under different conditions

From above experiment results, AC/2GA DES showed the best desulfurization performance, and therefore it was used to implement a series of control experiments to investigate the influence of different reaction conditions. Firstly, the temperature effect was investigated during oxidation desulfurization process of DBT. As shown in **Fig. 4**, it was observed that, when the temperature varied from 40 to 60 °C, the conversion of DBT remarkably increased from 32 to 99% in 3 h. However, the reaction activity was not significantly improved when the temperature further increased to 70 °C. A possible reason is the non-productive decomposition of H₂O₂ at the higher reaction temperature [31,39]. Therefore, taking into consideration of economic efficiency and energy consumption, 60 °C is selected as the optimum reaction temperature. The effect of H₂O₂/S molar ratio on the oxidative desulfurization reaction was also investigated at 60 °C (**Fig. 5**). It is well established that 2 mol of H₂O₂ are required for the oxidation of 1 mol of DBT to corresponding sulfones. However, when O/S molar ratio was 3, the sulfur removal was only 88% in 180 min. It was probably caused by the existence of the decomposition of H₂O₂, which is a competitive reaction of the oxidation process [48,49]. As expected, the O/S molar ratio has a remarkable influence on the desulfurization efficiency. When an increase of H₂O₂/S molar ratio was from 4 to 6, the sulfur removal increased obviously from 88% to 99%. Further increasing the O/S ratio to 7, the reaction rate was no longer sensitive to the H₂O₂/S ratio with sufficient H₂O₂ dosage. The explanation could be that the

Table 2
Effect of Different Desulfurization System on DBT Removal.

Entry	Name	HBA	HBD	Interaction energy (eV) between solvent molecules	Interaction energy (eV) with DBT	Sulfur removal (%)	
						EDS ^a	ECODS ^b
1	2AC/GA	AC	GA	-1.499	-0.610	21 %	57 %
2	AC/GA	AC	GA	-0.744	-0.592	19 %	95 %
3	AC/2GA	AC	GA	-1.058	-0.739	15 %	99 %
4	AC/3GA	AC	GA	-1.850	-0.878	13 %	95 %
5 ^c	—	AC	—	—	—	12 %	8 %
6 ^d	—	—	GA	—	—	7 %	60 %

Reaction conditions: ^aModel diesel (S content of 500 ppm, 10 mL), DESs (2 mL), T = 60 °C, t = 30 min.

^bModel diesel (S content of 500 ppm, 10 mL), DESs (2 mL), T = 60 °C, t = 3 h, n(H₂O₂)/n(DBT) = 6.

^cModel diesel (S content of 500 ppm, 10 mL), AC (0.3654 g), n(H₂O₂)/n(DBT) = 6.

^dModel diesel (S content of 500 ppm, 10 mL), GA (1.6346 g), n(H₂O₂)/n(DBT) = 6.

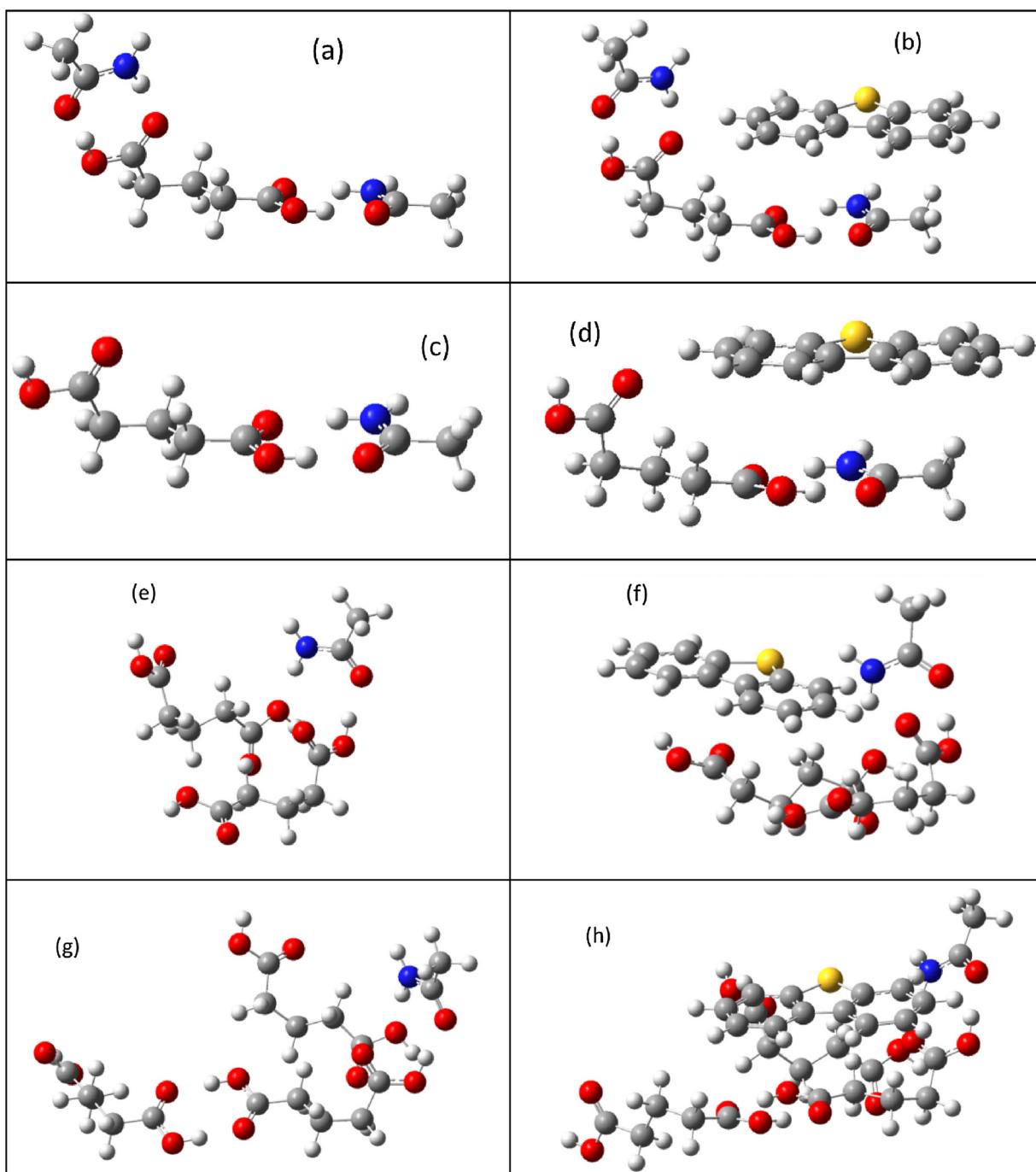


Fig. 2. The optimized structures of acetamide interacted with glutaric acid in the ratio of 2 : 1(a), 1 : 1(c), 1 : 2(e), and 1 : 3(g), respectively, as well as these clusters interact with DBT (b, d, f, and h).

introduction of a large amount of water may change the reaction system. Taking into account the economy, $\text{H}_2\text{O}_2/\text{S} = 6$ was selected as the optimal value.

To study the oxidative desulfurization efficiency for different sulfur compounds, a comparative investigation of the three sulfur containing compounds BT, DBT and 4,6-DMDBT was undertaken. As demonstrated in Fig. 6, the reaction activity decreased in the order of DBT > 4,6-DMDBT > BT, which may be ascribed to steric hindrance and electron density on the sulfur atom [50]. Otsuki et al [51] calculated that the electron densities of sulfur atoms in BT, DBT and 4,6-DMDBT were 5.739, 5.758 and 5.760, respectively. It is generally recognized that the higher the electron density of sulfur atoms, the easier the sulfide is oxidized. Therefore, 4,6-DMDBT should have the highest reactivity.

Beyond expectation, the DBT removal can reach to 99% in 3 h, which is significantly higher than that of 4,6-DMDBT (71%). This is probably due to two methyl groups of 4,6-DMDBT, which bring steric hindrance effect. Therefore, the reactivity of 4,6-DMDBT is lower than that of DBT.

3.4. Possible mechanism studies of the DBT oxidation process

In order to research the catalytic oxidative desulfurization mechanism, infrared spectroscopy was performed to give insight into the nature of interaction between the DES and DBT. The IR spectra in the region of 500 to 1200 cm^{-1} for DES, DBT, and their mixture at a molar ratio of 1 : 1 were shown in Fig. 7. The three fading bands at 744, 735,

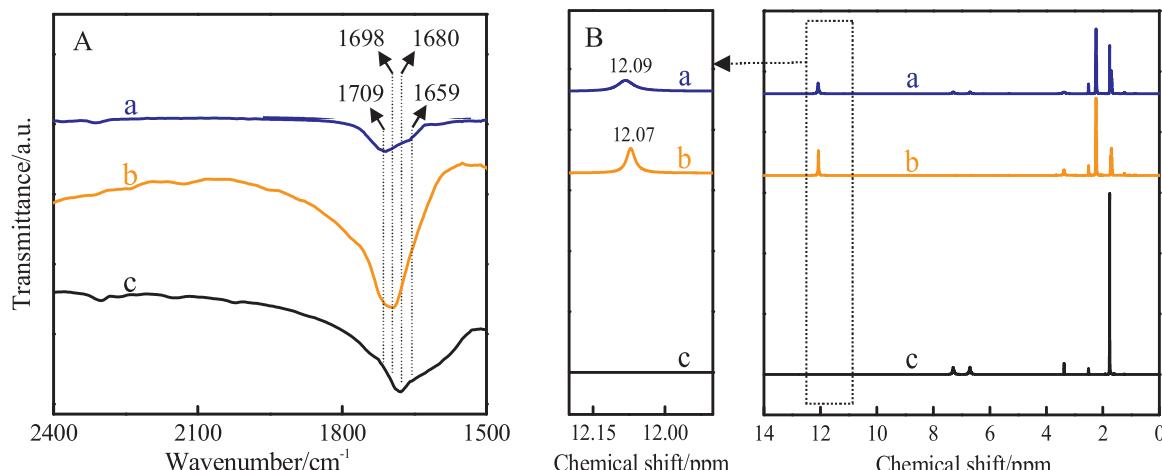


Fig. 3. (A) FT-IR and (B) ¹H NMR spectra of the GA/AC with the molar ratio of 2 (a), GA (b), and AC (c), respectively.

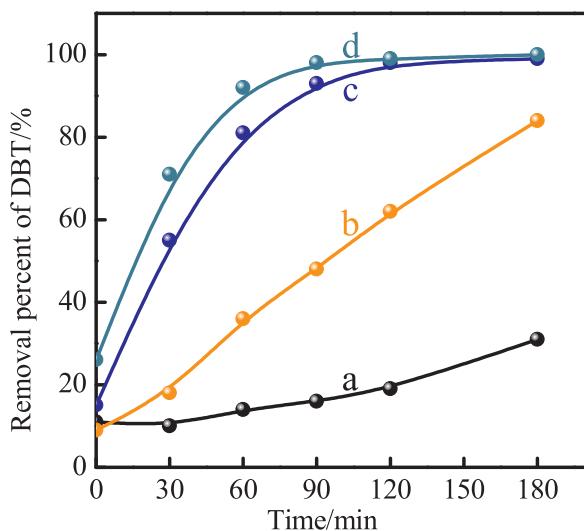


Fig. 4. Catalytic performances for the DBT removal at the temperature of 40 °C (a), 50 °C (b), 60 °C (c), and 70 °C (d), respectively. Experiment conditions: DES = 2 mL, model oil (DBT) = 10 mL, DBT (S content of 500 ppm) in *n*-octane, O/S = 6.

and 702 cm⁻¹ in DBT inferred that there might be a strong interaction after mixing DBT with DES [52].

Subsequently, GC-MS analysis was carried out to detect residual sulfides and reaction products in ECODS system, further to speculate probable catalytic oxidative mechanism. After reaction, the upper layer (oil phase) was decanted and analyzed directly by GC-MS. The lower layer (DES phase) was extracted by CHCl₃, and then the resulting CHCl₃ solution was measured by a GC-MS detector. The GC-MS analysis results of the oil phase and CHCl₃ phase are shown in Fig. 8(A) and (B), respectively. In oil phase, only *n*-octane and *n*-tetradecane could be found and no corresponding peaks of sulfur species appeared, indicating that sulfides were removed from oils phase completely. In contrast, a very tiny DBT peak at 18.32 min and the strong peak corresponding to DBTO₂ (*m/z* = 216.0) at 25.82 min was found in the CHCl₃ phase. The results indicate that the DBT was extracted into the DES phase firstly, and then was oxidized to DBTO₂.

According to some previous work, the acids are first oxidized by H₂O₂ to a peroxyacid when organic acids were used as catalysts, and then the DBT is oxidized to sulfoxide intermediates by a peroxyacid and then to final sulfone product. At the same time, the reduction of peroxyacid to carboxylic acid [30,31,37,38]. Using the DFT tool, we first study the reaction mechanism of DBT oxidation with glutaric acid as

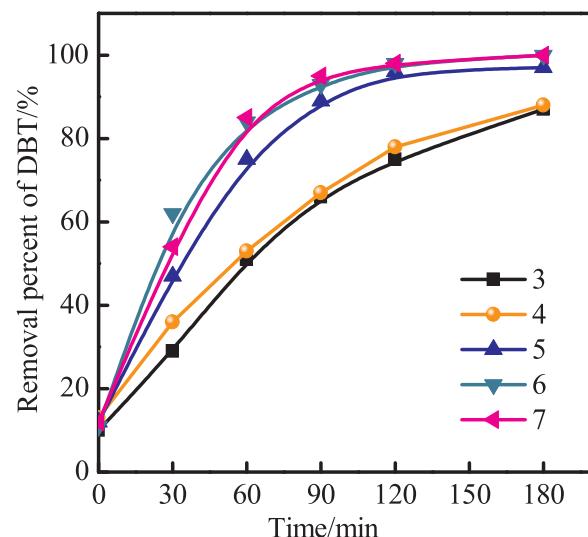


Fig. 5. Effect of different H₂O₂/S molar ratio on DBT removal. The number in this figure indicates H₂O₂/S molar ratio. Experiment conditions: T = 60 °C, DES = 2 mL, model oil (DBT) = 10 mL, DBT (S content of 500 ppm) in *n*-octane.

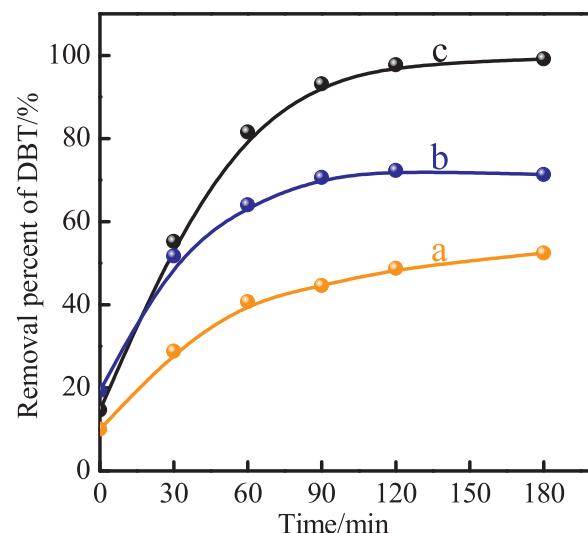


Fig. 6. The time-dependent catalytic activity for BT (a), 4,6-DMDBT (b), and DBT (c), respectively. Experiment conditions: T = 60 °C, DES = 2 mL, model diesel (S content of 500 ppm) in *n*-octane.

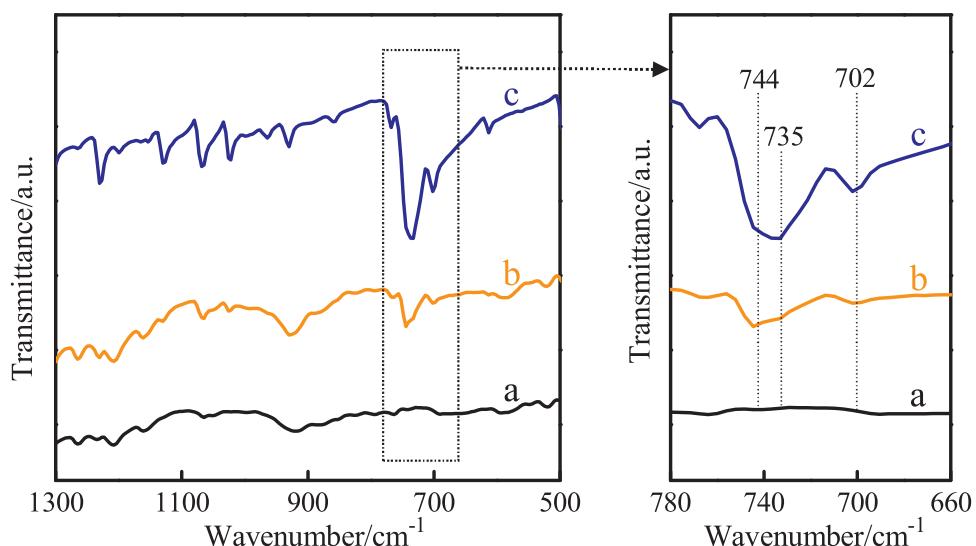


Fig. 7. Infrared spectroscopy of DES (a), the mixture of DES and DBT with the equal molar ratio (b), and DBT (c), respectively.

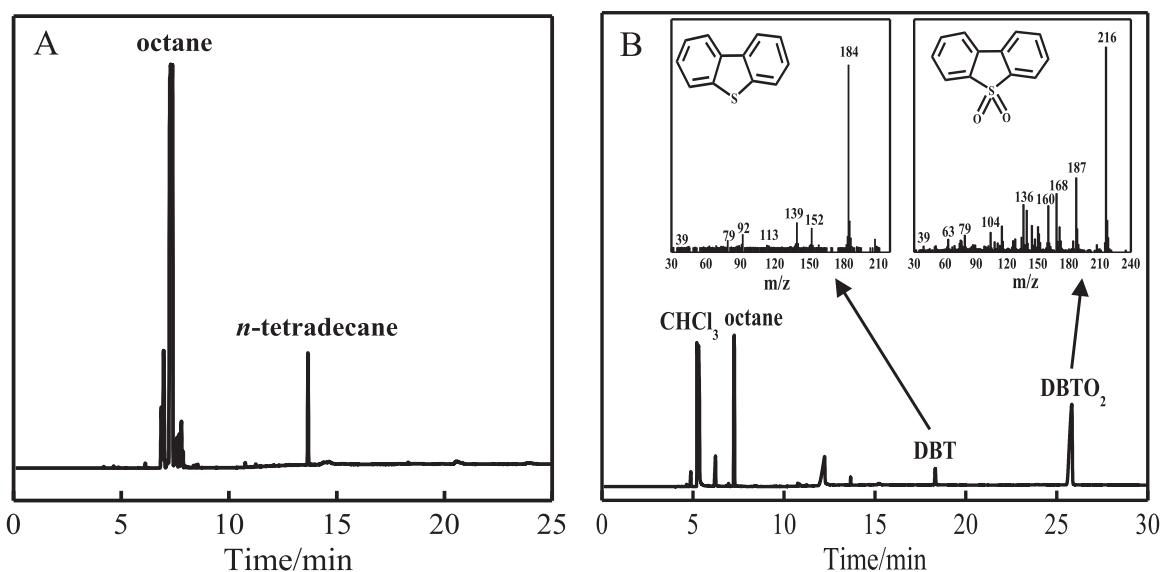


Fig. 8. The GC-MS of main compounds of the oil phase (A) and DES phase (B) after reaction.

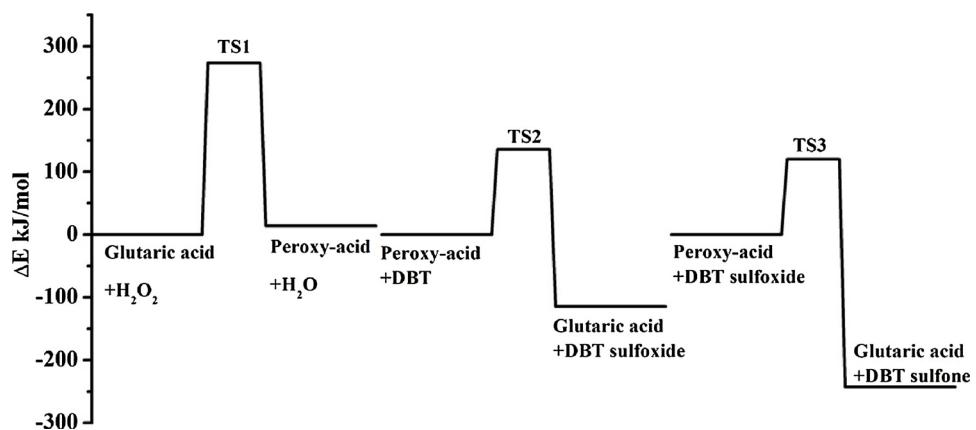


Fig. 9. The potential surface of DBT oxidized by H_2O_2 with glutaric acid as catalyst.

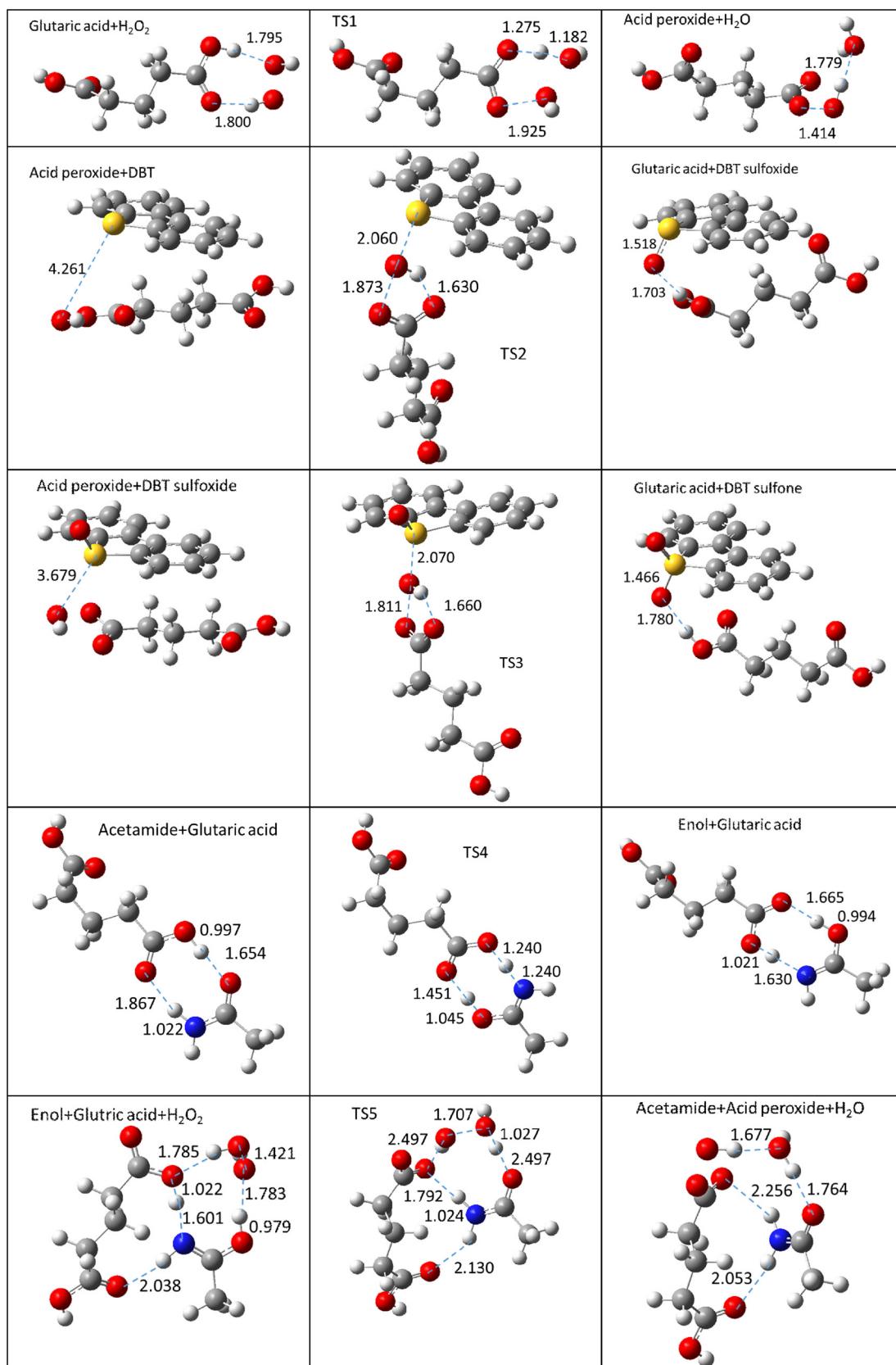


Fig. 10. The optimized structures of reactants, TS and products of H₂O₂ oxidation of DBT in DES of glutaric acid and acetamide.

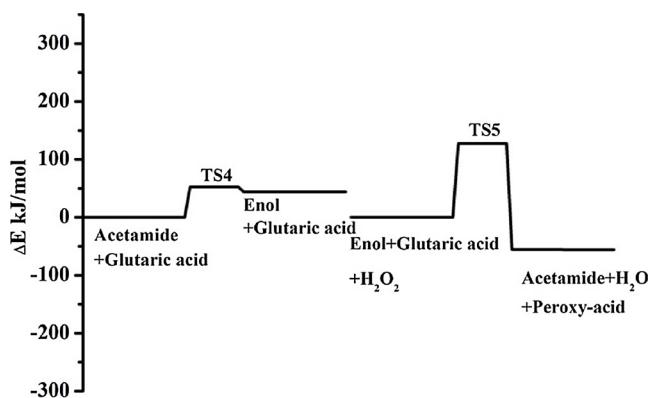


Fig. 11. The reaction potential energy of oxidation of glutaric acid with assistance of acetamide.

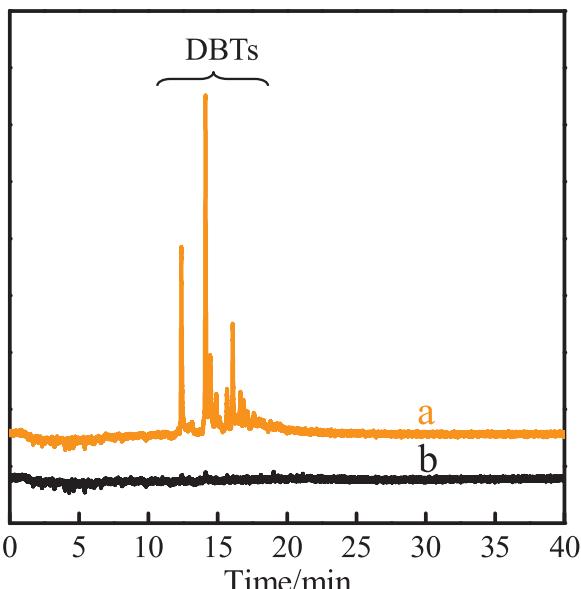


Fig. 12. GC-FPD chromatograms of original and desulfurized diesel with S content of 24 ppm (a) and 5 ppm (b), respectively.

the catalyst. The reaction potential surface is showed in Fig. 9. And the optimized reactant, transition-state (TS) and product are shown in Fig. 10. Interestingly, the transition state barrier (273.4 kJ/mol) of glutaric acid oxidation is much higher than the oxidation of DBT. Thus the oxidation of glutaric acid to peroxy-acid is actually the rate limited step. It is observed that the reaction barrier of 120.2 kJ/mol of DBT sulfoxide is lower than the 135.7 kJ/mol of DBT. This illustrates that sulfoxide is only an intermediate, which is oxidized further to final sulfone product under reaction conditions.

Due to that oxidization of glutaric acid is detected as the rate limited step, we further investigated how the acetamide influences this oxidation reaction. The results are shown in Fig. 11 and the optimized structures are shown in Fig. 10. It notes that the transformation of acetamide to ethyleneimine-2-nol can apparently decreased the reaction barrier of H_2O_2 oxidation of glutaric acid. By the two step reactions, the TS potential drops down from the original 273.4 kJ/mol to 127.2 kJ/mol, access to the TS of oxidation of DBT and DBT sulfoxide, thus enhancing the reaction activity.

Based on the results of FT-IR, GC-MS analyses and DFT, a proposed mechanism can be described as follows. During the reaction process, DBT is first extracted into the DES phase, and the aromaticity of DBT is weakened by the strong interaction between DBT and DES. At the same time, the $-COOH$ in acetamide/ glutaric acid DES can be oxidized into

peroxycarboxyl groups with H_2O_2 . It is interesting that the introduction of acetamide decreases the reaction barrier of H_2O_2 oxidation of glutaric acid. This means that acetamide/glutaric acid DES as efficient enzyme-like catalyst facilitates the oxidation reaction process [42,53]. Firstly, the acetamide can reduce the transition potential of peroxide of glutaric acid from 273 kJ/mol to 127 kJ/mol with an enol-like intermediate. Then the glutaric acid peroxide oxidize the DBT to DBT-O sulfoxide and then to DBT-O₂ sulfone with an energy barrier about 136–120 kJ/mol. The synergy cooperation of acetamide and carboxylate, which likes the active site of enzyme, achieves the highly catalytic oxidation performance of DBT. The DBT was firstly transferred from oil phase to DES phase, then oxidized to DBTO₂ continuously, and finally sulfur-free model oil was obtained.

3.5. ODS of real diesel fuel

In order to accurately test the practical applicability of the DES, a commercial diesel was chosen as a fuel feedstock with an original S content of 24 ppm. As shown in Fig. 12, almost no S-compounds were detected in the GC-FPD chromatogram after 3 h. The sulfur content decreased from 24 to 5 ppm with 79% sulfur removal. The S-removal efficiency results further ensured that the DES system was a robust and efficient oxidative desulfurization system for real diesel.

4. Conclusion

In summary, a series of acidic DESs was prepared by precisely mixing acetamide and glutaric acid with different molar ratios under mild conditions. Both experiments and DFT calculation indicated that acetamide/ glutaric acid (molar ratio 1 : 2) eutectic mixture are more stable and presents the highest catalytic activity in the ECODS system. This implied that the molar ratios of DESs were closely related to desulfurization activities. Furthermore, acetamide/ glutaric acid DES as efficient peroxidase mimetics reduced greatly TS barriers of glutaric oxidation by H_2O_2 , the rate determining step, and facilitated the reaction process for ODS. Finally, a proposed reaction mechanism was also proved by DFT and GC-MS systematically. The peroxidase mimetics concept mentioned above may provide useful guidelines on the improvement of ECODS activity and a new deep insight for understanding of the intrinsic properties of the DES.

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